TWO-STEP MECHANISM FOR ORDER-DISORDER KINETICS IN SILICATES

ROBERT F. MUeller, Goddard Space Flight Center, Greenbelt, Maryland 20771.

ABSTRACT

It is proposed that the apparent high activation energy barrier associated with the lower temperature limit $T_r$ of cation ordering in certain silicates is attributable to a mechanism involving two consecutive steps in the ordering process. This mechanism is regarded as responsible for certain ordering characteristics which distinguish metamorphic, igneous plutonic, and volcanic pyroxenes. An important consequence is that order-disorder equilibrium can be attained at temperatures below $T_r$ only through recrystallization and not by thermal annealing which does not result in recrystallization.

INTRODUCTION

The kinetics of ionic intracrystalline exchange (order-disorder phenomena) is an important aspect of the thermal behavior of minerals. The recent experiments of Virgo and Hafner (1969) have indicated that the high temperature kinetics of order-disorder in orthopyroxene are consistent with a simple exchange model which had earlier been found applicable to metallic alloys (Dienes, 1955) and which has been adapted to silicates (Mueller, 1967). However Virgo and Hafner (1969) also made the important observation that there is an apparent cut-off or transition region on the temperature scale below which no more ordering or disordering occurs. They attributed this behavior to an unmeasured energy barrier different from the one which is operative above the cut-off temperature of approximately 480°C in orthopyroxene and which has a measured activation energy of about 20 kilocalories in the direction of disordering.

It is apparent that the postulated energy barrier which is operative below the cut-off range is sufficiently high to prevent ordering even on a geological time scale since natural pyroxenes of slowly cooled metamorphic rocks still possess considerable disorder (Ghose, 1964). As was pointed out by Virgo and Hafner, the 20 kilocalorie barrier is not sufficiently high to prevent such ordering and cannot account for the relatively narrow cut-off temperature region. Further, since natural cummingtonites from metamorphic rocks also show considerable disorder (Ghose, 1961), it is likely that a similar cut-off or transition in mechanisms applies in this case and other cases also. It is obvious however that the transition temperature $T_r$ need not be the same in all silicates.
MECHANISM OF CONSECUTIVE STEPS

Two alternatives suggest themselves for the change of kinetic mechanisms which appears to be required to explain the ordering cut-off temperature $T_{\text{Tr}}$. These are: (1) a two consecutive step mechanism involving a low temperature process with a high activation energy and a high temperature process with a lower activation energy, and (2) two competing processes. We shall adopt the first alternative and show later why the second alternative does not apply.

The exchange kinetics of species such as Mg$^{2+}$ and Fe$^{2+}$ in a quasibinary crystal of the type of orthopyroxene may be represented by the following second order rate equation:

$$\frac{-dx}{dt} = \frac{1}{2} C_0[K_{12}\phi_{12}X_1(1 - X_2) - K_{21}\phi_{21}X_2(1 - X_1)].$$  (1)

In this equation $X_1$ and $X_2$ are the site occupancy fractions of either of the ionic species of a binary pair in the sites 1 and 2 respectively (represented in orthopyroxene by the symbols $M(1)$ and $M(2)$), $K_{12}$ and $K_{21}$ are the disordering and ordering rate constants, while $\phi_{12}$ and $\phi_{21}$ are corresponding factors analogous to activity coefficient products in macroscopic systems, except that they also contain the thermodynamic properties of the activated state. $C_0$ is the total concentration (in moles or atoms cm$^{-3}$) of both sites 1 and 2. In the case of completely ideal solutions, including both the stable lattice sites and the activated state sites $\phi_{12} = \phi_{21} = 1$ and Equation (1) reduces to its simplest form.

The potential energy relations which are reflected in the experimental activation energies and which are the chief contributors to the temperature sensitivity of the $K\phi$ factors may be represented as in Figure 1. This figure in particular is intended to refer to the exchange process above the temperature $T_{\text{Tr}}$ as manifested in such experiments as those of Virgo and Hafner (1969). In the latter case the average experimental activation energies $E_{\text{ex12}}^*$ and $E_{\text{ex21}}^*$ which correspond to $\Delta U_{12}^*$ and $\Delta U_{21}^*$ for disordering and ordering were found to be approximately

$E_{\text{ex12}}^* = 20$ kilocalories

$E_{\text{ex21}}^* = 16$ kilocalories

The cut-off temperature $T_{\text{Tr}}$ can be best explained by resorting to two consecutive processes with potential energy configurations as depicted in Figure 2. In this figure the high temperature ($H$) activated state cor-
responds to the 20 kilocalorie barrier discovered in orthopyroxene by Virgo and Hafner while the low temperature \((L)\) activated state corresponds to the barrier assumed to be operative below the cut-off temperature \(T_T\). According to kinetic theory (Glasstone, Laidler and Eyring, 1941) the system must pass over the highest barrier but need not pass through the intermediate state.

The mechanism of two consecutive reactions cannot however be explained solely on the basis of potential energy diagrams such as Figure 2 or the corresponding experimental activation energies. Kinetic theory tells us that the absolute reaction rate constants \(K_{12}\) and \(K_{21}\) are determined by the Gibbs free energy of activation \(\Delta G^*\) (Glasstone, Laidler and Eyring, 1941) since

\[
K = \nu \frac{kT}{h} \exp \left(\frac{-\Delta G^*}{RT}\right).
\]  

In this expression \(\nu\) is the transmission coefficient, \(k\) is Boltzmann's con-
Fig. 2. Potential energy diagram for the inferred consecutive two-step exchange process. The $L$-energy barrier is assumed to be in control at low temperatures while the $H$-barrier is assumed to be in control at high temperatures. The latter barrier also corresponds to that of Fig. 1.

stant, $h$ is Planck's constant, and $R$ is the gas constant. An additional relation is

$$\Delta G^* = \Delta H^* - T\Delta S^*,$$

(3)

where $\Delta H^*$ and $\Delta S^*$ are the enthalpy and entropy of activation respectively. In condensed systems such as this $\Delta G^*$ will not differ greatly from $\Delta F^*$ the Helmholtz free energy of activation and $\Delta H^*$ is consequently very similar to $\Delta E^*$ the internal energy of activation. Also these latter values should be similar in magnitude to the experimental activation energy $E^*_{\text{ex}}$.

The transmission coefficient in Equation (2) is difficult to evaluate and in the absence of any evidence to the contrary is usually set equal to unity. However it is clear from Equations (2) and (3) that even if $\Delta H^*$, $\Delta E^*$ and $E^*_{\text{ex}}$ are small $\Delta G^*$ may be indeterminately large depending on $T$ and $\Delta S^*$, assuming that $\Delta S^* < 0$.

The possible effect of different values of $\Delta G^*$ and $E^*_{\text{ex}}$ on the rate constants and their temperature sensitivities is depicted in Figure 3. Since the initial state is the same for both high and low temperature processes and since the high temperature process appears to be governed by the simple second order rate Equation (1), we may assume that the equation for the low temperature process has the same form and that only the
values of the $K\phi$ factors of the two processes will differ throughout most of the temperature range. However it is postulated here that the $K\phi$ factors for the two processes have the same value at the cut-off temperature $T_{Tr}$.

In consecutive processes the over-all rate is governed by the step for which $K\phi$ has the lowest value. Consequently below $T_{Tr}$, $K_L\phi_L < K_H\phi_H$ while above this temperature $K_H\phi_H < K_L\phi_L$. We may also imagine another diagram analogous to Figure 2 but with $\Delta G^*$ plotted instead of the potential energy. In such a diagram the height of the barrier would change drastically with the temperature so that in the high temperature range the $H$ barrier would be higher than the $L$ barrier. In this way it is possible to explain why at these temperatures only parameters such as $E^*_{ex}^H$ which refer to the high temperature process are registered. It is interesting that the negative value of the entropy of activation which is required for the high temperature process has been postulated on other grounds (Mueller, 1969).

Below the cut-off temperature where $K_L\phi_L$ is in control the temperature sensitivity of this rate constant is so great that it decreases rapidly.
such low values that the exchange process is frozen even on the cooling time scale of metamorphic rocks. Thus it is possible that in a temperature interval of less than 100°K the value of \( K_L \) decreases some orders of magnitude. Although no data are as yet available for a quantitative calculation, it is possible to get a qualitative impression of the effect by substituting certain values of \( K_L \) and the temperature interval. Thus from the general relation

\[
\frac{\partial \ln K_L}{\partial T} = \frac{E_{ex}^L}{RT^2},
\]

where \( E_{ex}^L \) is regarded as constant we obtain the integrated expression

\[
\ln \frac{K''}{K'} = \frac{E_{ex}^L}{R} \left( \frac{1}{T'} - \frac{1}{T''} \right),
\]

where \( K'' = K_H \) at \( T'' = T_{tr} \).

If for any temperature interval \( \Delta T = T'' - T' = 100^\circ K \) and \( T'' = T_{tr} = 753^\circ K \) (480^\circ C), and if we take \((K''/K'_L) = 10^6\) we find that \( E_{ex}^L \approx 140,000 \) calories. It is obvious that in a smaller temperature interval or for a larger change in \( K_L \) \( E_{ex}^L \) would be even larger.

**Exclusion of the Competing Mechanism**

In a mechanism involving competing processes the governing process of the over-all rate is that which occurs most rapidly. This situation is depicted in Figure 4, which is a schematic drawing analogous to Figure 3. It is clear from this figure however that a mechanism involving competing processes is incapable of explaining the observations in any simple way since the low temperature process involves a less steep slope below \( T_{tr} \), than that of the high temperature process. Consequently it is impossible for a great decrease in ordering (and disordering) rates to occur below \( T_{tr} \).

**Nature of the Low Temperature Process**

So far we have merely interpreted the observed ordering cut-off temperature as resulting from a two step mechanism without identifying the atomistic behavior responsible. Because of the inferred high activation energy for the low temperature process it seems likely that bond breaking is involved. Perhaps also this process involves the activation of vacancies which are inferred to play an important role in particle migration in crystal lattices (Dienes and Damask, 1965). Unfortunately it is impossible to characterize the kinetics in any greater detail than this now and it is likely that this will be possible only after extensive experimental work in the temperature range of \( T_{tr} \).
Fig. 4. Required relation between the rate factor for two competing mechanisms. Full lines indicate temperature ranges in which the rate factors govern the observed rate.

**Geological Consequences**

Some consequences of the experimentally determined kinetic behavior of orthopyroxene have already been pointed out by Virgo and Hafner (1969), but others come to our attention by considering the theoretical model. The general behavior of such silicates may best be summarized by a schematic diagram such as that of Figure 5. This figure illustrates the extent of attainment of heterogeneous and homogeneous equilibrium in the variety of environments encountered in natural samples.

It is clear first of all from Figure 5 that the macroscopic intercrystalline exchange equilibrium (line a) may in principle be attained and quenched in at any temperature at which crystallization or recrystallization can occur and merely reflects the latest of such events. However the establishment of this equilibrium requires the extensive reconstruction of the crystals involved except when unmixing occurs on dimension scales of some tens of microns as a maximum (Mueller, 1969). For example an intercrystalline distribution established at solidus temperatures in a plutonic igneous rock can only be destroyed by recrystallization at a lower temperature such as might be induced by shearing stresses. On the other hand the corresponding intracrystalline exchange equilibria of
such rocks (line b) will not ordinarily be quenched in at any temperature because of the slow cooling rate. The same conclusion also applies to metamorphic rocks (line c) above the temperature $T_{Tr}$. However in these rocks the attainment of the intracrystalline equilibria is possible below $T_{Tr}$ if crystallization or recrystallization occurs at these temperatures. The basis for this conclusion is that the establishment of the intracrystalline distributions should generally occur more readily than those between crystals (Mueller, 1969).

There is of course a slight probability that some igneous plutonic and metamorphic silicates could have their intracrystalline distributions quenched in above the temperature $T_{Tr}$, as is indicated by the dashed lines. This could occur for example if a recrystallizing metamorphic rock were cooled rapidly by introduced water along a fracture.

Only in volcanic rocks however is there a high probability for quenching of the intracrystalline distributions and such distributions were indeed measured by Ghose and Hafner (1967). This characteristic is indicated by line d in Figure 5.

The lower segment of line c is particularly interesting because it indicates that if a slowly cooled crystall such as a metamorphic orthopy-
roxene crystallized or recrystallized above $T_r$, the observed distribution of $\text{Mg}^{2+}$ and $\text{Fe}^{2+}$ between the $M$ sites all approximate the equilibrium distribution at $T_r$, except that $T_r$ itself is likely to vary somewhat as a function of compositional details. Thus it is unlikely that a suite of metamorphic orthopyroxenes define an equilibrium isotherm in detail.

Acknowledgments

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References

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